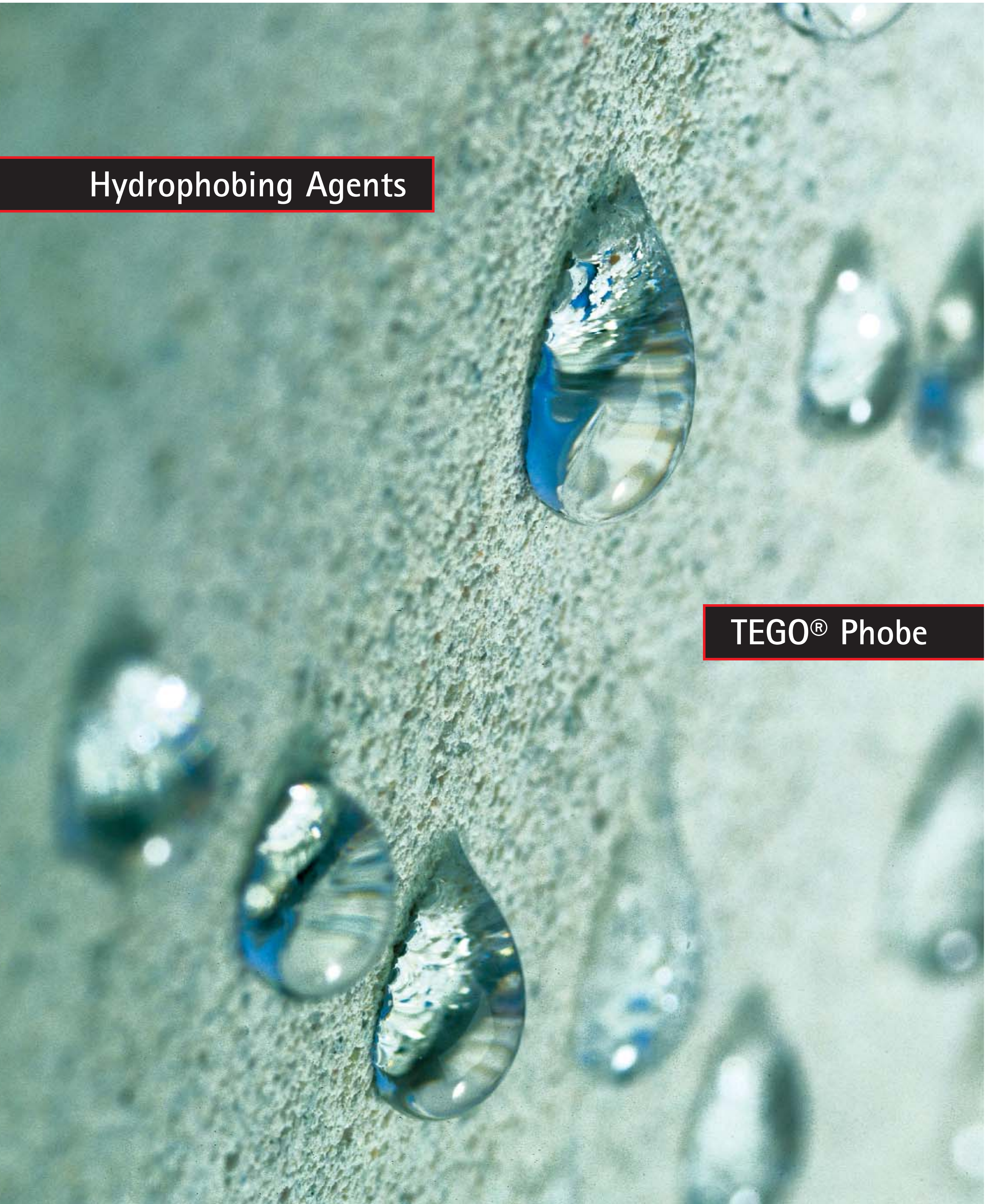
Hydrophobing Agents

TEGO® Phobe



Because of their pore and capillary structure, mineral building materials absorb moisture on contact with water. The absorbed water often results in visible damage and is also a carrier for harmful substances. Furthermore it acts as a reaction medium for destructive physical, chemical and biological processes which are deleterious to structures, disfigure external walls and severely impair their function. However with appropriate measures, surfaces exposed to the weather can be made water-repellent.

Figure 1: Inadequate permeability to water results in damage to facades.

Since ancient times, coatings have been considered effective protection for buildings. For such coatings to be durable, they should absorb as little water as possible but also exhibit good permeability to water vapor.

Systems with a high binder content and a PVC (pigment volume concentration) less than 50 % are the most frequently used as exterior paints. Because of their very low permeability to water vapor, blisters are frequently formed and the coating spalls (fig. 1).

Breathable silicate paints are equally lacking in providing lasting protection because their high water uptake can rapidly lead to damage. Only hydrophobing substances, which can be used in paints and as impregnating agents and primers, offer optimum protection and enable the manufacture of systems such as silicone resin and hydrophobed silicate exterior paints which both breathe and are water-repellent.

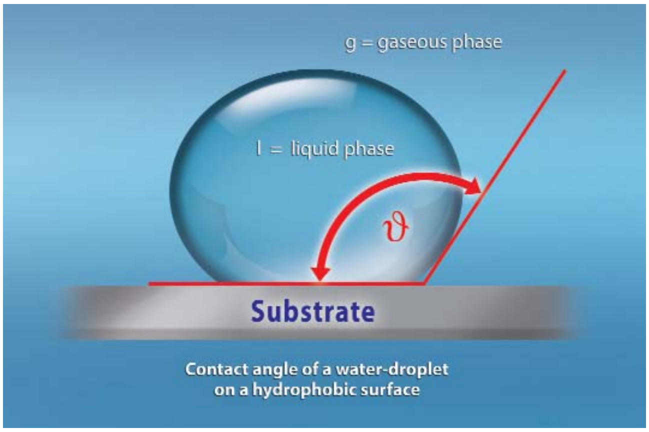


Figure 2: Contact angle

What is hydrophobicity?

In coatings technology, a substrate surface is described as hydrophobic or water-repellent if it is not (or not fully) wetted by drops of water on it. An important parameter characterizing hydrophobicity is the contact angle θ. It can be determined using droplets of water of constant volume applied to the surface (fig. 2 and video "Measurement of contact angle").

Particularly high contact angles are found for polyfluorocarbon and silicone-treated, highly water-repellent surfaces. The contact angles between water and such surfaces are between 140° and 160°. Contact angles are measured using an instrument which automatically determines the tangents at the substrate/liquid/air interface.

Interpretation of the measured contact angle does not, however, enable conclusions to be drawn on the internal water repellency, i.e. on the success or otherwise of an internal hydrophobing agent.

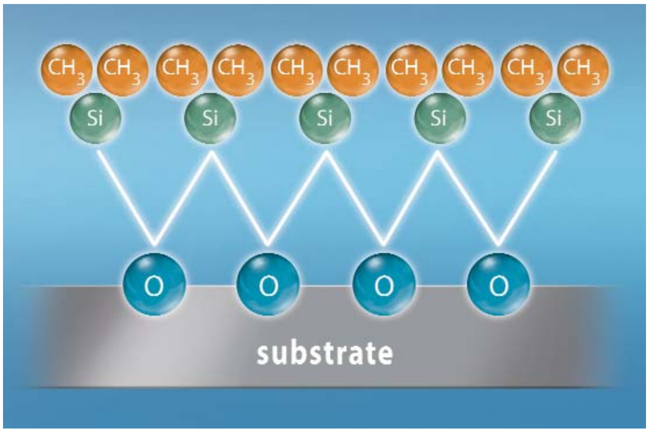


Figure 3: Activity of silicones on mineral substrates

It is just a measure of the beading effect of a surface. Measurement of the water absorption, the w_{24}-value, remains essential for evaluating internal hydrophobing.

Hydrophobing of surfaces

Silicones and paraffins are both substances which can make a surface hydrophobic. The differences lie less in the achievable contact angles than in their adhesion to the substrate. Silicones are particularly strongly anchored to mineral substrates via a Si-O-Si-linkage and can remain effective for decades. They spread easily over the surface. Silanes, in particular, also penetrate well into the substrate. Paraffins, in contrast, remain on the surface and the effect is often only temporary.

Silicone coatings are permeable to air and water vapor, and the porosity of the building material is almost or completely unaffected. Water cannot penetrate into the pores because the silicone increases the interfacial surface tension. It is thus possible to manufacture coatings based on silicones which are both water-repellent and able to breathe.

The degree of hydrophobicity achievable depends on the orientation of the molecules of the hydrophobing agent in relation to the substrate. Organopolysiloxanes arrange themselves in such a way that the oxygen atoms of the siloxane groups orient towards the substrate surface. The alkyl groups attached to the silicon atoms of the siloxane groups aggregate to form a densely packed outer layer. Increasing the packing density raises the hydrophobic effect (fig. 3).

The hydrophobic effect achieved with silicones is thus influenced by the type of substituents attached to the silicon atoms. Accordingly, the property profile can be controlled by, for example, the choice of alkyl groups.

Hydrophobing of facade systems

Facade protection systems can be made water-repellent by various methods. Impregnating the building material reduces water uptake to a minimum without affecting permeability to water vapor and carbon dioxide. For impregnation with siloxane products, Degussa offers TEGO® Phobe 6000 as well the waterborne products TEGO® Phobe 6500 and 6600.

Impregnation is certainly the most suitable method of protecting building materials which will not be further coated but it is not suitable for those with no or very low absorbing power.

Impregnating agents are only suitable for use as primers for coatings if they can penetrate deeply into the building material; otherwise overpainting may be problematical. The effect of the primer on the efficacy and longevity of coatings is often underestimated. An effective primer protects the coating from infiltration by damaging salts and water. In

Figure 4: Penetration of a primer into limestone

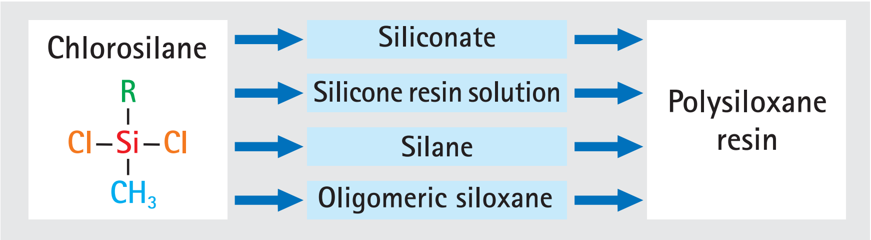


Figure 5: Chemistry of silicone products

the event that the top coat is damaged, the primer must also prevent water penetrating the building material and protect it from further damage.

Organic polymers, such as paraffins and polyolefin waxes, but also stearates, cannot be used as primers for coatings due to problems with adhesion and inadequate penetration (fig. 4).

Siloxanes, such as TEGO® Phobe 6000 and the waterborne TEGO® Phobe 6500, have, however, performed well. Another way of preventing undesired water absorption by the building material is to apply the hydrophobing agent as a component of the coating. In this type of hydrophobing, the coating reduces its water absorption by itself. Organosilicon compounds are ideally suited for this purpose. Degussa offers numerous such products which are described in detail below.

Chemistry of silicone products

All silicones are manufactured from chlorosilanes (cf. "Technical Background: Silicone Resins and Silicone Combination Resins"). A broad spectrum of properties can be achieved by varying the alkyl groups bound directly to the silicon atom. Methyl groups, for example, result in products which are very durable when applied to neutral or slightly alkaline substrates. If, on the other hand, longer chain organic substituents are used, the resulting products provide long-lasting water repellency on strongly alkaline substrates.

Different types of silicone hydrophobing agents can be manufactured by reacting the chlorosilanes with various other reactants.

Siliconates

Siliconates are highly alkaline solutions. They react with atmospheric carbon dioxide (CO_2) to form silanols which then react with each other to produce a polysiloxane resin. Methyl or propyl potassium siliconates are used almost exclusively. However, reaction with CO_2 also produces potassium carbonate which is deposited as a salt on the surface.

Silicone resins

As there are problems using siliconates for hydrophobing facades, silicone resins are normally employed. Their molecular weights lie between 2,000 and 3,000 and are therefore very low compared to those of organic resins. Because of their relatively small molecular size, silicone resins can penetrate into the pores and capillaries of building materials significantly better than organic resins.

Silanes

Silanes have been used since the early days of silicone chemistry to render mineral substrates water-repellent. They are produced by reacting chlorosilanes with alcohols. Their particular advantage over already cured silicone resins (see below) is their greater depth of penetration in building materials because of their smaller molecular size.

First of all, the silane reacts with moisture in the air or building material to give a silanol which then forms a silicone resin via a condensation reaction. This reaction does not take place spontaneously but requires a certain amount of time which depends on the environmental conditions. To achieve an acceptable reaction rate, alkylmethoxysilanes are used. Undesirable side effects are the evaporation of the highly volatile silane and the elimination of alcohol.

Oligomeric siloxanes

Combined alcoholysis/hydrolysis (that is reaction with alcohol and/or water) of chlorosilanes results in low molecular weight silanes (oligomers) which exhibit many advantages such as good penetration even of moist substrates and the almost complete absence of vapor pressure so that they do not evaporate. Curing occurs by humidity as in the case of silanes. The siloxane oligomers combine the advantages of silicone resins and silanes. Because of their sensitivity to water, however, they cannot be used in today's common waterborne coatings. Amino-functional oligomers are used as additives for hydrophobing coatings.

After evaporation of the solvent (water and or organic solvent), the water-repellent effect is fully developed. Curing of the resin occurs through condensation of the remaining reactive groups.

Facade protection theory

Despite the hydrophobic effect just described, coatings are never completely impermeable to water or water vapor. For facade protection, it is also necessary for a mineral building material to be able to breathe to a certain extent, a situation comparable with that of a GoreTex® membrane in an otherwise rainproof jacket.

In Künzel's Facade Protection Theory, two properties of the coating significantly influence protection and breathability characteristics. These are the water absorption capacity of the building material and the water vapor permeability of the coating. Because of the protective effect of the coating, transport of water vapor from the exterior to the interior is very slow. This is a diffusion process, the rate of which is strongly dependent on the concentration gradient between the substrate and the surrounding air.

The s_d-value

According to Künzel, there is a quantitative relationship between the water repellency of a coating and its permeability to water vapor. In this, two parameters, the s_d-value and the w-value, play key roles. The s_d-value is the thickness in meters of a hypothetical static air layer which would have the same resistance to water vapor diffusion as the coating or building material. It is calculated from values of water vapor diffusion measured according to EN ISO 77832. For a coating film, this depends on the coating thickness and the pigment content, i.e. the PVC. s_d-values for coatings range from less than 0.1 m for the most water vapor permeable films (silicate paints) to about 2 m for coatings with poor porosity (solventborne acrylic paints).

The w-value

The w-value is a measure of the water absorption of a building material through its capillaries. It is calculated from the weight of the absorbed water in kilograms divided by the product of the surface area in square meters and the square root of the time.

$$\frac{kg}{m^2 \cdot \sqrt{24h}}$$

In an optimal coating system low water uptake and high water vapor permeability should be achieved. The following classifications are taken from the appropriate standards:

Water permeability coefficient

(EN ISO 1062-3)

Class	Water uptake	w-value $\frac{kg}{m^2 \cdot \sqrt{24h}}$
III	low	< 0.1
II	medium	0.1 – 0.5
I	high	> 0.5

Water vapor diffusion

(EN ISO 1062-3)

Class	Water vapor diffusion	s_d-value m
I	high	< 0.14
II	medium	0.14 – 1.40
III	low	> 1.40

Facades protected with coatings meeting these criteria lose more water when drying than they absorb when being wetted by rain. Hydrophobic coatings fulfill the requirements in terms of both vapor permeability and behavior in capillary absorption, and are therefore the highest quality products on the market (fig. 6). The performance of the hydrophobic coatings is nearly ideal in this regard.

For a coating to have a high water vapor permeability requires high porosity which results in a low s_d-value. To achieve this, the pigment concentration, symbolized by PVC (pigment volume concentration), must exceed a certain boundary value, known as the critical PVC (CPVC). The CPVC can be altered by manipulation of the amount and nature of the pigments and fillers as well as by the choice of binder.

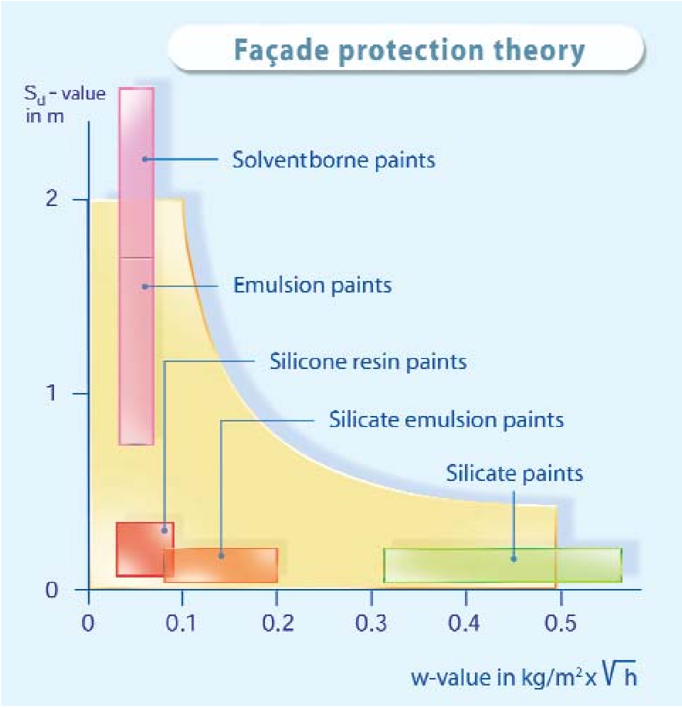


Figure 6: Façade protection theory (according to Künzel)

The high porosity increases the natural ability to absorb water and coatings so formulated must therefore be made hydrophobic with appropriate agents.

Measuring water vapor permeability by the wet-cup method

Water vapor permeability is determined gravimetrically to EN ISO 7783-2 using a low reactivity (inert) substrate. The substrates are 60 mm diameter borosilicate glass frits. The coating is applied uniformly onto the frit with a flat brush. When the first coat is dry, a second is applied. The coating is allowed to dry overnight under constant conditions (23 °C, 50 % relative humidity) followed by 24 hours at 50 °C. The resulting dry film thickness should be between 150 and 200 µm.

A glass weighing dish with a diameter of 61 mm and a height of 30 mm is filled with 20 ml of distilled water. Before the coated frit is placed on the dish, a sponge is placed in the dish. This prevents liquid water from coming into contact with the coated side of the frit, as this could otherwise invalidate the measurement. The frit and weighing dish are sealed with hot melt adhesive. The prepared weighing dish is then weighed on an analytical balance (± 0.1 mg), and is stored in a climatic chamber for five days and then weighed again. The difference between the two weights gives the amount of water vapor diffused (fig. 7). The detailed procedure of this method please see in the video "Measurement of water vapour diffusion (s_d-value)" on the enclosed CD-ROM.

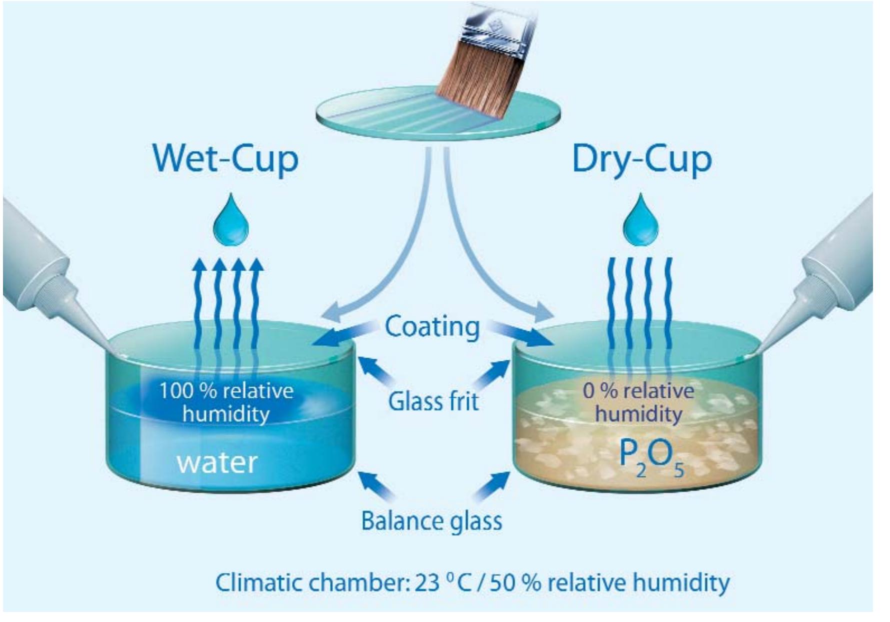


Figure 7: Wet-cup method

Comparison of the wet-cup method and the dry-cup method

In the wet-cup method the direction of diffusion goes from the 100 % relative humidity inside the weighing bottle to the 50 % relative humidity in the climatic chamber. In the dry-cup method the direction is reversed: from 50 % relative humidity in the climatic chamber to 0 % relative humidity inside the weighing dish. The relative humidity of 0 % is obtained by using a sufficient quantity of phosphorus pentoxide (P_2O_5).

Because the amount of water diffused in the wet-cup method is larger by a factor of ten, it is more accurate and is therefore more widely used than the dry-cup method.

Measuring capillary absorption of water

The capillary water absorption is determined to DIN EN 1062-3. The test substrate is a block of calcium sandstone measuring 115 x 70 mm (= 0.008 m^2) with a thickness of 20 mm. The cut blocks are thoroughly scrubbed under water and then dried for 24 hours at 50 °C.

The paint is applied by pouring it onto the block and spreading with a flat brush. One of the two largest sides and the four sides adjoining it are coated. All the pores of the block must be filled in.

The prepared dry test blocks are placed coated side down on foam in a tub filled with water. The water level must reach the lower side of the test blocks. The level must therefore be checked from time to time, and the water replenished.

After 24 hours, the blocks are removed, laid on paper and patted dry. DIN EN 1062-3 requires that the test sample be exposed three times to wash out the water soluble components of the coating; the w_{24}-value is then obtained from a fourth exposure. Please also see the video "Measurement of water absorption (w-value)" on the CD-ROM.

The w-value is defined as the weight of the absorbed water in kilograms divided by the product of the surface area in square meters and the square root of the time.

For example: If the rate of water absorption were 0.5 kg water/m² in 24 hours, the w-value would be:

$$w_{24}\text{-value} = \frac{0.5}{\sqrt{24}} = \frac{0.5}{4.9} \approx 0.1 \frac{kg}{m^2 \cdot \sqrt{24h}}$$

The accuracy of the w-value increases with the thickness of the coating. As long as the barrier effect of the coating remains intact, the w-value is independent of the coating thickness as absorption by the substrate becomes less important.

Emulsion or silicate-emulsion based coatings intended as protection for mineral building materials must have s_d- and w-values as low as possible.

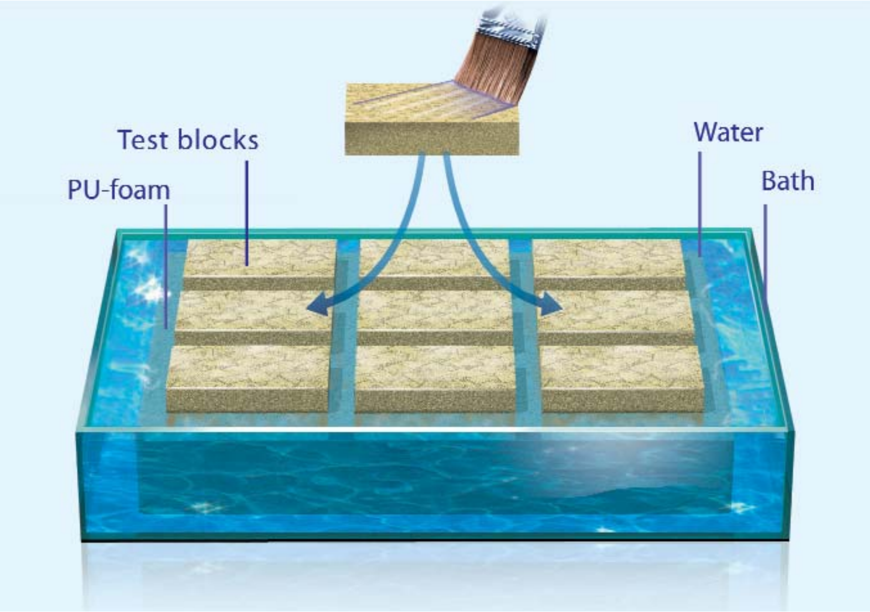


Figure 8: Measuring of water absorption

Hydrophobing agents for facade coatings

Silicate emulsion paints and plasters

Formulating with silicates gives the advantage of silicating the substrate as well as providing excellent water vapor permeability but unfortunately leads to high water absorption. The optimal formulation therefore requires addition of a hydrophobing agent which inhibits water absorption without affecting water vapor permeability. Several TEGO® Phobe products are available for this purpose. Formulation of a silicate emulsion paint:

Formulation of a silicate emulsion paint

Component	Weight-%	Ingredient/effect	Suppliers
Water	20.25		
Walocel CRT 10000 PV	0.25	Cellulose	www.wolff-cellulosis.com
Kronos 2130	9.80	Titanium dioxide	www.kronos.de
Mowiplus XW 330	0.20	Wetting and dispersing agents	www.clariant.com
Betolin Quart 20	0.50	Waterglass stabilizer	www.woellner-silicat.de
TEGO® Foamex 825	0.20	Defoamer	www.tego.de
Omyacarb 1 AV	7.40	Calcium carbonate	www.omya.com
Omyacarb 5 GU	22.10	Calcium carbonate	www.omya.com
Plastorit 000	4.90	Talc	www.luzenac.com
Mowilith DM 765	8.80	Styrene acrylate	www.celanese.com
Betolin P 35	19.60	Silicate (Waterglass)	www.woellner-silicat.de
White spirit	1.00	Film forming agent	
Betolin A 11	1.00	Viscosity stabilizer for silicate	www.woellner-silicat.de
TEGO® Phobe 1401	4.00	Hydrophobing agent	www.tego.de
	100		

Silicone resin paints and plasters

Using a combination of silicone and organic resin emulsions all the requirements made on a breathing coating can be fulfilled: good water vapor permeability, low water absorption, good adhesion, low-stress film, resistance to atmospheric influences, algae and fungus, easy processing and quick drying. Combination with a TEGO® Phobe silicone resin additionally gives good driving rain resistance and very good color development with commercial tinting concentrates. The solvent-free and highly-effective emulsion TEGO® Phobe 1650 is recommended for these applications. TEGO® Phobe 1000 and 1000 S are further products containing a very limited amount of organic solvent

Emulsion paints with silicate character (SIL-paints)

Because they are formulated using quartz powder or other mineral fillers, these paints have a particularly open cell and capillary-active structure and are therefore permeable to water vapor.

Formulation of a silicone resin paint

Components	Weight-%	Ingredient/effect	Suppliers
Water	25.40		
Bentone LT	0.30	Thickener	www.elementis-specialties.com
TEGO® Foamex 835	0.20	Defoamer	www.tego.de
Parmetol A 28	0.15	Preservative	www.schuelke-mayr.com
Calgon N new	0.05	Water softener	www.bk-giulini.com
TEGO® Dispers 715 W	0.40	Wetting and dispersing additive	www.tego.de
AMP 90™	0.10	Neutralizing agent	www.dow.com/angus
Kronos 2310	12.50	Titanium dioxyde	www.kronosww.com
Socal P 2	10.00	Calcium carbonate	www.solvay.de
Omyacarb 5	15.00	Calcium carbonate	www.omya.com
Omyacarb 2	10.00	Calcium carbonate	www.omya.com
Glimmer Mica TG	3.00	Mica	www.quarzwerke.com
Aluminiumsilikat P 820	2..00	Aluminium silicate	www.degussa.com
TEGO® Phobe 1650	7.20	Hydrophobing agent	www.tego.de
Dowanol DPnB	1.00	Film forming agent	
Acronal 290 D	12.00	Styrene acrylate	www.basf.com
Rheolate 278	0.70	PU-thickener	www.elementis-specialties.com
	100		

The increased capillary water absorption which also occurs can be inhibited by TEGO® Phobe 1401 without affecting the water vapor permeability.

Siloxane facade coatings with water-beading effect

The water-beading effect of siloxane facade coatings is considerably increased by suitable hydrophobing agents in combination with a special surface texture. The desired micro-rough surface texture is achieved using Sibelite® M 3000 or Calcimatt. In addition to very low water uptake, the coating is also characterized by excellent water vapor permeability.

All the raw material components should have as low an emulsifier content as possible and have no hydrophilic properties: the water-beading effect is significantly impaired, for example, if polyacrylates or polyphosphates are used as wetting agents.

Emulsion paints and plasters

The organic emulsion binders inhibit water absorption by emulsion coatings and plasters. Additional hydrophobing or water-beading can be achieved by addition of TEGO® Phobe 1401 and TEGO® Phobe 1500 N.

FAQs

Rain causes vertical tracks to occur which are different from the original color. How can this sensitivity of a freshly applied silicone resin facade coating to sudden rain be improved?

TEGO® Phobe 1650 produces so-called early water resistance. Using this, the values specified in DIN for incorporation

Formulation of an emulsion paint with silicate character

Component	Weight-%	Ingredient/effect	Suppliers
Water	13.85		
Walocel XM 30000 PV	0.20	Cellulose	www.wolff-cellulosics.com
NaOH, 10 %	0.15		
TEGO® Dispers 715 W	0.30	Wetting and dispersing additive	www.tego.de
Calgon N, 10 %	1.00	Wetting and dispersing agents	www.bk-giulini.com
TEGO® Foamex 855	0.30	Defoamer	www.tego.de
Kronos 2160	10.00	Titanium dioxide	www.kronos.de
China Clay Grade B	5.00	Kaolin	www.imerys.com
Mica MU-N 85	5.00	Mica	www.zieglerco.de
Sikron SF 500	10.00	Quartz	www.quarzwerke.com
Sikron SH 300	20.00	Quartz	www.quarzwerke.com
Quartz powder W 10	7.50	Quartz	www.quarzwerke.com
Dowanol DPnB	1.20	Film forming agent	www.dow.com
TEGO® Phobe 1401	2.00	Hydrophobing agent	www.tego.de
Mowilith DM 2452	23.00	Styrene acrylate	www.celanese.com
TEGO® ViscoPlus 3030	0.30	PU-thickener	www.tego.de
Acticid MBS	0.20	Preservative	www.thor.com
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Formulation of a siloxane facade coating with water-beading effect

Components	Weight-%	Ingredient/effect	Suppliers
Water	22.85		
TEGO® Foamex 825	0.20	Defoamer	www.tego.de
Surfynol E 104	0.30	Wetting and dispersing agents	www.airproducts.com
Walocel XM 6000 PV	0.40	Cellulose	www.wolff-cellulosics.com
Acticid MBS	0.10	Preservative	www.thor.com
Kronos 2044	20.00	Titanium dioxide	www.kronos.de
Sibelite® M 3000	32.00	Quartz (Christobalit), 14µm	www.quarzwerke.com
or Calcimatt		Calcium carbonate, 20µm	www.omya.com
Ammonia 25 %	0.15	Neutralizing agent	
Acronal 290 D	5.00	Styrene acrylate	www.basf.com
TEGO® Phobe 1500 N	9.00	Hydrophobing agent	www.tego.de
Acronal 290 D	10.00	Styrene acrylate	www.basf.com
	100		

Note that in this formulation a portion of the styrene acrylate emulsion is added to lower the viscosity before the incorporation of the hydrophobing agent.

into color class I are already almost achieved after the first exposure to water (four exposures to water are required in DIN).

Does the silicone resin in silicone facade coatings affect the s_d-value and is the PVC of the coating altered?

The s_d-value remains unchanged and the silicone resin does not have to be included as part of the binder in calculating the PVC.

On storage for 5 - 6 months our silicone resin paints show a sharp increase in viscosity. How can this be prevented?

The order of additions when manufacturing a paint plays an important role. After manufacturing the mill-base the silicone resin emulsion should be added first of all. Only then can the binder be added. The choice of wetting and dispersion agent is also of decisive importance. Ammonium-neutralized polyacrylates have proved particularly good for long period storage stability.

In manufacturing a facade paint with marked water-beading effect using TEGO® Phobe 1500 N, we have noticed a significant increase in viscosity. How can this be avoided?

Because TEGO® Phobe 1500 N is a resin solution in a film formation agent, increases in viscosity can occur. In contrast to the silicone resin emulsions, which are added after manufacture of the mill-base, about 1/3 of the binder should be added *before* addition of TEGO® Phobe 1500 N. After that the rest of the binder dispersion can be incorporated.